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(71) Sökande Sandvik AB, Sandviken SE  
Applicant (s)

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REGISTRERINGSVERKET  
SWEDEN

Postadress/Adress  
Box 5055  
S-102 42 STOCKHOLM

Telefon/Phone  
+46 8 762 25 00  
Vx 08-762 25 00

Telex  
17978  
PATOREG S

Telefax  
+46 8 666 02 86  
08-666 02 86

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Huvudfaxen Kassan

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## **SURFACE MODIFIED STAINLESS STEEL**

### **FIELD OF THE INVENTION**

- 5 The present invention relates to a stainless steel, which after nitriding exhibits a hardened surface layer with a hardness of at least 1200 Hv and which is particularly useful in applications with high demands on a combination of high strength and/or toughness and wear resistance and as substrate for coating.

### **10 BACKGROUND OF THE INVENTION**

- Stainless steel alloys are relatively less hard than other steel materials. As a result in many applications the stainless steel article or part is provided with a hardened surface, often referred to as case hardening. The concept of case  
15 hardening is to transform a relatively thin layer of material at the surface of the part by enrichment of carbon or other ingredients to make the surface harder than the matrix of the alloy, where matrix is the of the surface modification unaffected part of the steel. The steel thus retains in bulk the desired formability of stainless steel without the softness of the matrix at the surface of modified  
20 steel.

- Stainless steels are often casehardened by carburization. Carburization is a process by which carbon atoms are diffused in solution into the surface of the article. Known case hardening processes are performed at high temperatures. However, carburization processes performed at temperatures greater than  
25 about 540°C (for stainless steel alloys) can promote the formation of carbides in the hardened surface.

- Plasma nitriding is an alternative case-hardening process, which is carried out in a glow discharge in a nitrogen gas-containing mixture at a pressure of 100 to 1000 Pa (1 to 10 mbar), is one of the used method to treat stainless steel  
30 surfaces, resulting in a nitrogen diffusion layer having high hardness and excellent wear resistance. Nitriding hardening is induced by the precipitation of nitrides in the surface layer.

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## DESCRIPTION OF THE RELATED ART

Plasma nitriding is the most recently developed surface hardening procedure.

5 The process replaces traditional nitriding methods, such as gas nitriding and nitrocarburization (short-term gas nitriding, bath nitriding and tenifer treatment) as identical thermo-chemical conditions can be established in this process. Plasma nitriding achieves higher hardness and wear resistance, while creating lower distortion.

10 Plasma nitriding is very cost effective. This is due to the fact that subsequent machining, finishing and residue-removal processes are frequently not required. Similarly, supplementary protective measures, such as burnishing, phosphatizing etc., under some conditions even galvanizing and hard-chrome plating, may not be necessary.

15 Plasma nitriding is performed in a vacuum furnace. Treatment temperatures in the range of 400 to 580°C are employed subject to the requirements of the process at hand. Typical treatment temperatures are in the range of 420 to 500 °C. The most commonly used process gases are ammonia, nitrogen,  
20 methane, and hydrogen. Oxygen and carbon dioxide are used in the corrosion-protective step of post-oxidation. Aside from the type of process gas used, pressure, temperature, and time are the main parameters of the treatment process. By varying these parameters, the plasma nitriding process can be fine-tuned to achieve the exact desired properties in any treated component.

25 Any iron-based material can be subjected to plasma nitriding. The process does not require the use of special types of nitriding steel.

The results achieved through plasma nitriding can be reproduced with pinpoint accuracy. This is especially important in the manufacture of serial products.

30 US 5,632,826 discloses a precipitation hardened martensitic alloy in which the strengthening is based on the precipitation of particles. The strengthening particles have a quasicrystalline structure, said structure being essentially

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obtained at aging times up to 1000 h and tempering treatments up to 650°C.  
This strengthening involves an increase in tensile strength of at least 200 MPa.  
It has now surprisingly been found that if steel according to US 5,632,826 is  
nitrided on the surface, an unexpected further increase in surface hardness is  
5 obtained in difference to the matrix of said stainless steel.

### SUMMARY OF THE INVENTION

It is therefore a primary object of the present invention to provide a stainless  
10 steel alloy characterized by increased hardness at the surface of said alloy after  
modification of the surface at the same time as the hardness of the matrix of the  
stainless steel is also increased.

Another object of the invention is to provide products made of said surface  
modified stainless steel.

15 An additional object of the present invention is to provide a stainless steel  
substrate for coating with wear resistant layers.

### BRIEF DESCRIPTION OF THE DRAWINGS

20 Fig. 1 shows a light-optical micrograph of the microstructure of one  
sample of the surface modified stainless steel according to the  
present invention in 500X, where A is the nitrided surface layer, B is  
the stainless steel matrix.

25 Fig. 2 shows the hardness (in Hv) plotted over the depth (in mm) from the  
surface.

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**DETAILED DESCRIPTION OF THE INVENTION**

The stainless steel substrate before surface modification according to the present invention has the following composition (in weight-%):

5	Carbon	max 0.1
	Nitrogen	max 0.1
	Copper	0.5 - 4
	Chromium	10 - 14
10	Molybdenum	0.5 - 6
	Nickel	7 - 11
	Cobalt	0 - 9
	Tantalum	max 0.1
	Niobium	max 0.1
15	Vanadium	max 0.1
	Tungsten	max 0.1
	Aluminum	0.05 - 0.6
	Titanium	0.4 - 1.4
	Silicon	max 0.7
20	Manganese	$\leq 1.0$
	Iron	balance

and normally occurring usual steelmaking additions and impurities.

25 Said stainless steel contains quasicrystalline particles in the martensitic microstructure as a result of a precipitation hardening.

Plasma nitriding is a surface hardening process, which utilizes the properties of gas plasma, i.e. an ionized gas, to achieve desirable mechanical properties at the surface of the work piece.

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The main influential parameters in nitriding are pressure, temperature, and time of treatment as well as the chemical composition of the ionized process gas.

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Plasma nitriding takes place at a vacuum pressure between 0.3 to 10 mbar. The actual treatment pressure chosen is governed by the geometry of the part and the desired surface layer structure.

5 The treatment temperature in the range of 400 to 580°C is selected according to the type of material and pre-treatment of the part and the desired layer structure. Treatment time varies between 10 minutes and 70 hours, and depends on the part to be treated as well as the desired structure and thickness of the layers formed. Plasma nitriding uses ammonia or gas mixtures containing methane, nitrogen, and hydrogen as the process gas. The process gas used is  
10 selected subject to the nature of the part to be treated and the required layer structure.

The invention also relates to a material treated with the method according to the present invention in form of wire, plate, strip, tube and pipe and other  
15 geometries, especially complex geometries for use in applications with high demands on a combination of high strength and/or toughness and wear resistance, such as e.g. wear parts of engines and other engine components, impact loads, such as safety devices, cam followers, cam follower pads, valve stems, valve stem guides, piston pins, piston shafts, hydraulic pistons, ejector  
20 pins, safety protection plates, lock cylinders and other locking devices, blocking elements, thief-proof equipment or the like.

#### EXAMPLE

25 The substrate as described earlier was subjected to a surface modification by a plasma nitriding process at 450 to 580°C during a period of time of 1 to 40 hours. This process obtains a hardening of the surface between 0.05 and 0.5mm. The hardening process can be carried out on wire, plate, strip, tube and pipe and parts with a wide variation of geometries, especially complex  
30 geometries. It is a special advantage of the stainless steel substrate used according to the present invention, that very complex geometries can be formed without any changes in dimension. The hardness of the surface is at least twice

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the hardness of the substrate 0.5mm into the matrix. It is at 1200 Hv, preferably at least 1100 Hv.

Figure 1 illustrates the hardness profile from the surface of the substrates into the matrix. It has unexpectedly shown that the hardening effect is visible down to 0.5 mm into the matrix. It is therefore considered being a big advantage of this combination of substrate and the method of surface treatment, that creates a surface modified material with a deep-hardened surface zone.

Thus, the surface modified stainless steel according to the present invention is particularly well suited for use as substrate for the deposition of a wear resistant coating.

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## Claims

1. Stainless steel with a composition as following (in weight-%):

5	Carbon	max 0.1
	Nitrogen	max 0.1
	Copper	0.5 - 4
	Chromium	10 - 14
	Molybdenum	0.5 - 6
10	Nickel	7 - 11
	Cobalt	0 - 9
	Tantalum	max 0.1
	Niobium	max 0.1
	Vanadium	max 0.1
15	Tungsten	max 0.1
	Aluminum	0.05 - 0.6
	Titanium	0.4 - 1.4
	Silicon	max 0.7
	Manganese	≤ 1.0
20	Iron	balance

Normally occurring usual steelmaking additions and impurities characterized in, that said stainless steel after nitriding exhibits a hardened surface layer with a hardness of at least 1200 Hv.

25 2. Stainless steel according to claim 1, characterized in, that said stainless steel contains quasicrystalline particles in the martensitic microstructure as a result of a precipitation hardening.

30 3. Method for the making of a surface modified stainless steel according to claim 1, characterized in, that said stainless steel is subjected to a nitriding process at 450 to 580°C during a period of time of 1 to 40 hours in a plasma nitriding atmosphere.



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4. Product according to any of the previous claims in form of wire, plate, strip, tube and pipe and other geometries, especially complex geometries for use in applications with high demands on a combination of high strength and/or
- 5 toughness and wear resistance, such as e.g. wear parts of engines and other engine components, impact loads, such as safety devices, cam followers, cam follower pads, valve stems, valve stem guides, piston pins, piston shafts, hydraulic pistons, ejector pins, safety protection plates, lock cylinders and other locking devices, blocking elements, thief-proof equipment or the like and without
- 10 change in dimension.
5. Material according to claims 1 and 2 use a substrate for the deposition of wear resistant coating.

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**Abstract**

The present invention relates to a stainless steel, which after nitriding exhibits a hardened surface layer with a hardness of at least 1200 Hv and which is in form  
5 of wire, plate, strip, tube and pipe and other geometries, especially complex geometries, particularly useful in applications with high demands on a combination of high strength and/or toughness and wear resistance and as substrate for coating.

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Figure 1

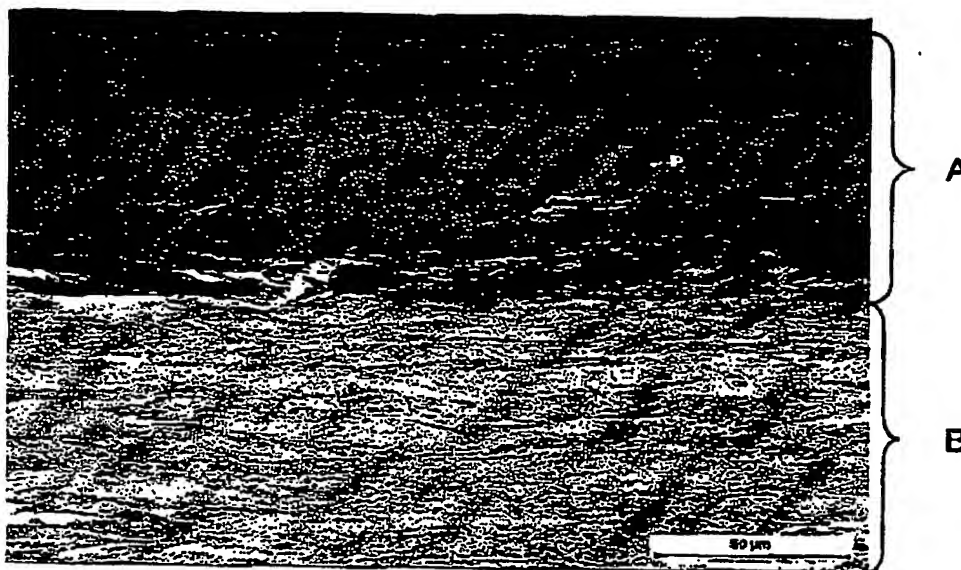
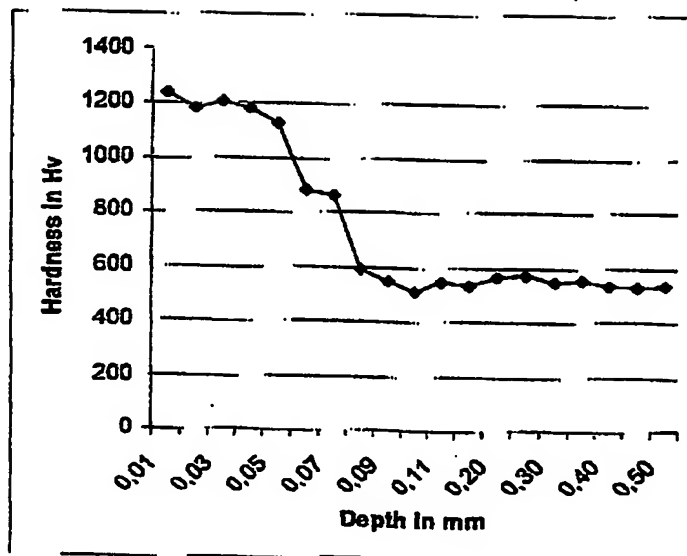


Figure 2



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